The University of Chicago

THE DETERMINATION OF THORIUM IN MONAZITE SAND BY AN EMANATION METHOD

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

HOMER HENRY HELMICK

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PART I

In a recent paper,[1] Cartledge described an "emanation method" for the determination of thorium in monazite sand which was based on the facts: (1) thorium is the first member of the series of radioactive elements now known as the thorium series; (2) one of the members of the series, thorium emanation, is a gas. As a further basis for his method, he assumed: (1) on account of the great age of monazite, the elements of the thorium series have reached "radioactive equilibrium," (2) in an acid solution of monazite sand, the emanation is in such a condition of availability that it can be practically completely swept out by bubbling air through the cold solution. In our work on this problem we have accepted the same facts and made the same assumptions.

Cartledge states that his method "by a triplicate analysis will give the thorium content within 1.5 per cent of its true value," and pointed out that the inability of the method to give results of a higher degree of accuracy was probably due to the adsorption of thorium *X* by the undissolved material in the final solution, by the filter paper employed in the process of making the solution, and on the walls of the vessels used. Assuming that he was correct as to the sources of error, it was obvious that a much greater degree of accuracy could be obtained if a method could be perfected which would produce a complete solution of the sand without filtration and which would require the use of but one vessel. A thorough study of this problem led to a very satisfactory solution.

PRELIMINARY WORK

It occurred to us that a fusion of monazite sand with a suitable flux might prove a satisfactory substitute for the acidified water solution used by Cartledge. Such a flux must give, with the sand, a melt from which the emanation can be continuously and quantitatively swept out by a current of air or other suitable gas. It was desirable that the temperature necessary for the fusion be less than 1000°, and that the fused mass be not too viscous, since it must be rapidly and thoroughly stirred by the gas bubbling through it.

In our search for a flux which would produce a melt having the properties mentioned above, we made fusions with three different

[1] *Journal Am. Ch. Soc.*, XLI (1919), 40.

fluxes and obtained results as shown in Table I. In each case 2.0 g. of sand were used with 20.0 g. of the flux and the mixture heated for one-half hour.

The fact that we were unable to sweep any emanation out of the $KHSO_4$ melt eliminated it from further consideration. The alkali carbonate melt was also abandoned because of (1) the considerable percentage of sand remaining undecomposed, (2) the violent effervescence which would make quantitative work difficult, and (3) the high temperature necessary. The fusion with HPO_3 appearing promising, a

TABLE I

Flux	Properties of the Melt				
	Viscosity	Appearance	Percentage of Sand Decomposed	Availability of Emanation	Temp.
Anhyd. HPO_3	About that of heavy oil	Liquid transparent and very light blue. Undecomposed material heavy and almost black	Over 99 per cent	Not investigated	About 700–800°
Anhyd. $KHSO_4$	Not much greater than that of water	Light yellow opaque mixture of solid and liquid. Undecomposed material heavy and dark. H_2SO_4 fumes given off	About 90–95 per cent	Rough tests seemed to show no availability	About 250°
Equal parts anhyd. Na_2CO_3 K_2CO_3	About that of light oil	Gray, opaque mixture of solid and liquid. Undecomposed material heavy and dark	About 50–75 per cent	Not investigated	900–1000°

rough experiment was performed to determine the pressure necessary to force a stream of air through the fused mass at a moderate rate. The fusion was made in a hard-glass flask. It was found that only a moderate pressure was necessary, but that the method was impracticable with the glass vessel, since it was rapidly attacked by the acid and also was so softened by the heat that, under the influence of the difference of pressure inside and out, a gradual but serious change in shape occurred in the time which would be necessary for a determination of the emanation.

Before obtaining a platinum vessel, which, it appeared, would be necessary, we decided to try to dissolve the cold melt in water. The possibility of success in that direction was suggested by a consideration of the chemical nature of the constituents of monazite sand and by the appearance of the cold mass. The first rough qualitative experiments proved so encouraging that we did not make further efforts to use the hot melt directly.

MAIN RESEARCH

1. THE SOLUTION

A fusion was made of twenty parts HPO_3 to one part of sand, and the heating continued for fifteen minutes after no further decomposition was observable. The melt was poured into a mortar and, after cooling, was ground to a powder. For convenience, we will call the product thus obtained melt 1.

Then 0.1 g. of melt 1 was shaken up for several minutes with about 20 c.c. water. No observable solution occurred. On warming to boiling, however, the material dissolved at a moderate rate, only a very slight, heavy, dark residue, probably ilmenite, remaining undissolved. On standing, the solution became turbid, and the turbidity increased on heating. Believing this precipitation to be due to the silica and silicates in the sand, two experiments were tried as follows: (1) 3.0 g. of sand were fused with 10.0 g. HPO_3 to which 2.0 g. of CaF_2 had been added; (2) 3.0 g. sand were treated with conc. hydrofluoric acid and evaporated to dryness. This operation was repeated three times, and then the sand was fused with HPO_3.

The ilmenite was decomposed by the hydrofluoric acid in both cases, and so the fusions were almost complete, but since titanium was evidently brought into solution but not removed, the water solutions were much more turbid than those previously made. So we have not again made use of hydrofluoric acid, but have tried, by adjustment of temperature and of acid concentration, to keep the silicon in solution, as far as possible, in the form of silicic acid.

Since heating seemed to be the cause of the formation of the precipitate on attempting to dissolve melt 1 in water, we decided to try cold hydrochloric acid as a solvent, 0.1 g. of melt 1 was shaken up with 10 c.c. of water and 10 c.c. of conc. HCl. The material, excepting, of course, the undecomposed part, dissolved completely in a few minutes. The solution was perfectly clear at first, but, after standing four or five hours, a turbidity became apparent, and, in two days, a distinct, though

slight, flocculent precipitate had developed. However, since for our purpose the solution would be used immediately after preparation, such a very slow precipitation would probably have no appreciable effect on our results.

Since Cartledge had shown that the best results could be obtained with solutions having a volume of 75 c.c. and containing 2.0–2.5 g. of sand, it remained to see whether we could duplicate those conditions: 10.0 g. of melt 1 (containing 0.5 g. sand) were placed in a flask and hydrochloric acid (equal parts conc. HCl and H_2O) added 10 c.c. at a time. After each addition the flask was violently shaken for several minutes. Solution gradually took place as more and more of the solvent was added, but, when a volume of 500 c.c. had been reached, a considerable percentage of the melt remained undissolved. Boiling, at this point, caused the entire mass to dissolve readily, but, as we had anticipated, a heavy flocculent precipitate was produced.

Consideration showed that our failure to get, in the cold, a solution of practical volume might possibly be due to any one or more of the following causes: (1) the very large excess of HPO_3 used in the fusion, (2) the wrong concentration of HCl in the solvent, (3) the wrong temperature.

The investigation of these possibilities was carried out as follows:

A fusion containing practically the minimum percentage of HPO_3 was made by adding finely ground sand, 1.0 g. at a time, to fused HPO_3 until the last portion added was decomposed only very slowly and with difficulty. The resultant melt contained 6.0 g. of sand and 20.0 g. of HPO_3. We will call the product melt 2.

A 1.0 g. portion of melt 2 was placed in each of eight flasks. Four of the flasks were placed in a water bath at 75–80°, while the other four remained at room temperature. The mixtures in all the flasks were agitated for three hours with 100 c.c. of solvent. The details of the experiment and the results obtained have been combined in Table II.

A review of these results showed that, if we wished to avoid the use of an impracticable volume of solution and an impracticable time for making it, we probably must be satisfied with solutions containing a slight precipitate. Since the sample 6 gave, in a reasonably short time, a solution containing only a small precipitate, we decided to use that treatment in making solutions for a series of trial determinations. Considering the fact that the precipitates in our solutions were much less than those present in solutions prepared by the method of Cartledge, we felt justified in making measurements to test the accuracy of our

method, especially since it did not involve filtration and required but one transfer of the solution.

It was now obvious that the cold melt would have to be ground up if we wished to dissolve it quickly. On account of the glasslike nature of the melt when cold, we believed it extremely difficult, if not impossible, with the apparatus at our disposal, to grind it up without losses which would be too great for a quantitative procedure. We therefore at this point abandoned the idea of dissolving the melt in water or hydrochloric acid, and began looking about for a more efficient solvent.

TABLE II

Temp.	Sample No.	Solvent	Approximate Time for Complete Solution	Approximate Amount Precipitate after 3 hours
15–20°	1	100 c.c. H_2O No HCl	Very long time, if at all	None
	2	67 c.c. H_2O 33 c.c. HCl	2 or 3 days, if at all	None
	3	33 c.c. H_2O 67 c.c. HCl	1 day	0.1 mg.
	4	No H_2O 100 c.c. HCl	1 day	1.0 mg.
75–80°	5	100 c.c. H_2O No HCl	1 day	0.1 mg.
	6	67 c.c. H_2O 33 c.c. HCl	2.5 hours	10.0 mg.
	7	33 c.c. H_2O 67 c.c. HCl	1 hour	100.0 mg.
	8	No H_2O 100 c.c. HCl	45 min.	100.0 mg.

Neglecting, for the moment, all consideration except speed of solution, it seemed that if we could find a solvent which contained a small percentage of H_2O and at the same time had a high boiling-point, we might, by use of a higher temperature, succeed in reducing the time to practical limits. Ordinary orthophosphoric acid immediately suggested itself as having the properties mentioned. So an experiment was carried out as follows:

A fusion was made in the usual manner, allowed to cool in the crucible, and 80 per cent H_3PO_4 added until the crucible was three-fourths filled. The crucible was then placed in a sand bath and kept at 240–50°, the liquid being continuously and rapidly agitated by a stirrer attached to a motor. After three hours the contents of the

crucible consisted entirely of a slightly viscous mass which could easily be poured out into a beaker, and it was found that the crucible could then be washed out clean with a little water. The addition of 50 c.c. of water to the material in the beaker produced, with the aid of a little stirring, a solution which was much less turbid than any which we had been able to get by the use of water and hydrochloric acid.

Eighty per cent orthophosphoric acid is, then, the most nearly ideal solvent for the melt which we have thus far found. Compared with other solvents investigated, it has the following advantages:

a) The production of a final solution containing only a very slight precipitate.

b) The solution of the melt in a comparatively short time.

c) A quantitative transfer of material from the crucible to the vessel in which the determination is to be made.

d) The production of a solution of ideal volume.

Trial determinations of thorium in monazite sand have therefore been made by the emanation method, using anhydrous HPO_3 as a flux and 80 per cent H_3PO_4 to dissolve the melt.

The details of the method and the results obtained are given in later parts of this paper.

2. APPARATUS

We have used with but slight changes and additions the electroscope and accessories set up by Cartledge. A full description is given in the paper mentioned above, and we will therefore describe only the new parts.

a) *Pressure regulator.*—Our method depends on comparing the rate of discharge of an electroscope by the emanation from a solution of the "unknown" sample with the rate of discharge by the emanation from a standard solution. In order that these rates may be comparable it is necessary that the speed with which the emanation is drawn from the solution into the ionization chamber be the same, within narrow limits, in both cases. The speed depends on the pressure gradient, and so a constant pressure gradient must be maintained along the line traversed by the air carrying the emanation. The atmospheric pressure at the point where the air enters the solution remains practically constant during the time necessary for a determination. It only remains, therefore, to maintain, in some part of the line farther from the solution than the ionization chamber, another point of constant pressure.

This we have done by introducing a short branch from the main line to a pressure regulator. Its relation to the rest of the set-up is shown in Figure 3. For a detailed drawing of the piece, see Figure 1.

Although the drawings show but two air inlets, the regulator used actually has seven. All of these inlets will admit air to the line under

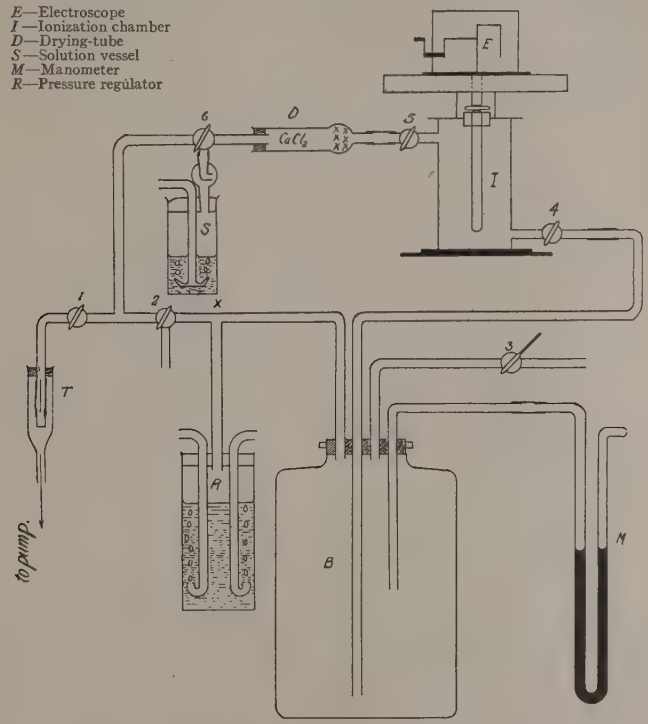


FIG. 3.—Diagram of set-up for emanation measurement

almost the same pressure conditions. In preparing to make a determination, cock 1 (see Fig. 3) is opened wide. Then cock 2 is opened slowly until the pressure in the line is so reduced that three or four of the seven inlets of the regulator are admitting air. The pressure at the point *X* will then remain practically constant, for, if the pressure becomes slightly greater some of the inlets will cease to admit air, while if the pressure becomes slightly less more of them will admit air.

We find that this simple device maintains the pressure constant to within 0.2 mm. of olive oil.

This regulator is a refinement of the Mariotte bottle. Although very simple, it is the result of considerable experimentation. Various types of inlet tubes which were tried and found insufficiently sensitive are:

1. Straight 1.0 mm. tubes, without jet.
2. Straight 5.0 mm. tubes, with and without jet.
3. Bent 5.0 mm. tubes, without jet.

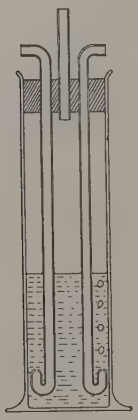


FIG. 1.—Pressure regulator.

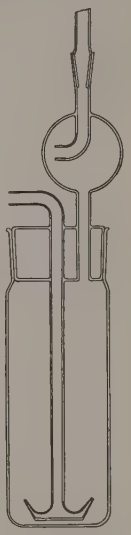


FIG. 2.—Solution vessel (actual size).

The liquid used in the regulator is water, and adjustment for any desired pressure is easily made by taking out or putting in water to obtain the proper height of the water surface above the jets of the inlet tubes.

b) *Solution vessel.*—After some experimentation, we have designed and used the solution vessel shown diagrammatically in Figure 2. It has the following advantages over any other we have used:

1. It is made of good glass and has an especially thin bottom, so that the very hot (200–50°) solution of the melt can be poured into it without danger. If the solution in the crucible is allowed to cool, it rapidly becomes too viscous to pour well.

2. It is tall and narrow. This is best for three reasons: (*a*) accuracy is possible in the reproduction of the same volume for successive solutions

by filling to a mark, (*b*) efficient stirring of the solution by the stream of air bubbles is attained, and (*c*) a relatively long time of contact of air bubbles with the solution and contact of each bubble with a considerable part of the solution are possible.

3. The ground-in glass stopper carrying the air-inlet tube. The inlet tube thus always reaches the same distance below the surface of the solution, and one source of variations in pressure gradient is thus avoided.

4. The stopper carries as a part of the outlet tube a trap to reverse the direction of flow of the air current, and thus any mechanically carried solution is prevented from reaching parts of the apparatus which are not subject to cleaning before each determination.

5. The bottom of the stopper is 6.5 cm. above the surface of the solution, so that only a negligible portion of the solution can be thrown against it by the bursting bubbles.

6. The bulb on the lower end of the inlet tube has eight jets on its upper side. Experience in making the pressure regulator showed this sort of inlet tube to be advantageous.

7. A ground-glass connection is made with the line to the ionization chamber. Rubber connections are liable to be a source of error on account of variable length, leakage, plugging, etc.

c) *Change in set-up.*—We have found it advisable to use a longer calcium chloride tube (*D*, Fig. 3), and to mount the manometer, *M*, and cock 3 on top of the telescope stand, where they are within easy reach and directly observable by the operator while seated at the telescope.

ENTIRE PROCEDURE FOR THE DETERMINATION

The sample.—About 50 g. of the well-mixed sand are weighed out and ground up until all has passed through a 100-mesh sieve.[1] It is then thoroughly mixed and placed in a weighing-bottle, and dried to constant weight at 115–20°. For a determination, a 2.0-g. sample is weighed out to within 0.001 g.

The fusion.—The sample is mixed by pouring back and forth between sheets of glazed paper, with 8.0 g. finely ground anhydrous HPO_3. Good quality HPO_3, recently fused and kept in a desiccator, is used. The mixture is placed in a 35-c.c. platinum crucible and fused by heating with a Mekar burner. The heat is applied slowly at first to avoid undue effervescence. After the highest temperature thus attainable is reached, the crucible is so manipulated that particles of sand which may be sticking to the sides are exposed for several minutes to the hot acid.

[1] One hundred wires per inch; equal to 40 per cm.

The heating is continued for one hour. Then, after removing the burner, the crucible is rotated by means of forceps in such a way that the mass, when cool, is distributed as evenly as possible over the surface of the lower half of the inside of the crucible. The cooled product is practically transparent, colorless, and glasslike.

Solution of the melt.—After allowing to cool for a minute or two, 20 c.c. 80 per cent H_3PO_4 is added to the crucible, and it is then placed in an air bath where it is heated up to 250–55° and maintained at that temperature for three hours. During that time it is stirred by a platinum stirrer attached to a motor. The liquid resulting from this treatment is, at 200–250°, about as viscous as light oil.

Transfer to solution vessel.—The solution vessel is suspended, to about one-third its depth, in a bath of concentrated H_2SO_4 at 190–200°. The stirrer is lifted just above the liquid in the crucible and rotated for a few seconds to free it of most of the liquid adhering to it. Then the liquid is quickly poured out of the crucible into the solution vessel. The latter is now taken out of the hot bath, placed on an asbestos board, and allowed to cool. Twenty c.c. water are run into the crucible, the liquid is stirred vigorously for a minute or two, and the washings are poured into the cooled solution vessel. This operation is repeated with a second 20 c.c. of water. Any heavy particles of undecomposed sand, usually a little ilmenite, still remaining in the crucible are then washed into the solution vessel by using 5 c.c. of water blown from a small wash bottle holding just that amount. The mixture in the solution vessel is now rapidly stirred for at least fifteen minutes. The same stirrer is used as before. Finally the stirrer is lifted just above the liquid, rotated for a few seconds and washed with 5 c.c. of water from the small wash bottle mentioned above, the wash water being caught in the solution vessel. Water is then carefully added to bring the volume of the solution up to 75 c.c., which is indicated by a line etched on the vessel. The stopper carrying the inlet tube is then fitted into the solution vessel. A little desiccator grease is used to insure an air-tight joint.

THE MEASUREMENT

(For diagram of apparatus see Fig. 3)

Measurements are made on three different solutions: the blank, the standard, and the "unknown."

The blank is run first. This solution may be used for an indefinite number of determinations. It is prepared according to the method for a regular sample except that the monazite sand is omitted.

The bottle containing the blank is attached to the line in place of the bottle, *S*, shown in the diagram. The pump is started, cocks 1, 3, 4, and 5 opened wide, cock 6 opened wide between *S* and *D*, and then cock 2 opened between cock 1 and *X*. Cock 3 is now gradually closed until half the inlets of the pressure regulator are admitting air. We have the regulator so adjusted that the manometer, *M*, which contains olive oil, then shows a difference between the pressure in bottle *B* and the atmospheric pressure, of 11.5 cm. (as per Part II). Under these conditions the air bubbles through the solution at a rate sufficient to stir it rapidly and thoroughly. The time of discharge of the electroscope is then noted.

The standard. Fresh $CaCl_2$ is placed in tube *D*. Cock 2 is turned so as to admit air through the side tube and close the line to the pump. The standard solution is substituted for the blank. Cock 6 is opened between the solution and the pump, and a moderate stream of air drawn through the solution for six minutes to rid it of RaEm. The cocks are then adjusted exactly as they were for the blank and readings of the time of discharge taken.

The "unknown." Treated exactly like the standard solution.

The ionization chamber is then evacuated for one-half hour and the pump stopped.

Results obtained.—Only four determinations have been made by the method outlined above, but the results were so encouraging that we feel

TABLE III

Sample No.	Discharge by Blank	Discharge by Standard	Discharge by Unknown	Percentage Thorium in Sand
	Min.	Sec.	Sec.	
50	101	197.6	187.9	8.61
51	60	192.3	184.5	8.57
52	93	190.5	183.9	8.52
53	85	198.7	191.4	8.54

justified in considering this method a distinct stage of improvement. The analyses were made with India monazite sand, No. 22. The results are shown in Table III. The percentage of thorium was calculated on the basis of the standard representing 8.22 per cent thorium.

PART II

In Part I the writer has described a way of determining thorium in monazite sand by means of a constant-flow emanation method. Although that method did not give the thorium content of the sand with the degree of accuracy usually desired, it was believed that further investigation would reveal modifications which would make the method sufficiently accurate to be of very distinct value. We have therefore carried out a series of experiments to determine more exactly the degree to which each factor affected the result of the determination and have devised means of controlling more accurately those factors whose variations were found to be responsible for the undesirable effects.

PROTECTION OF THE INSULATION

In Part I it was shown that a calcium chloride tube was inserted between the solution and the ionization chamber. Many experiments had shown that if the air current was not thus dried, the electroscope would be discharged erratically and always too rapidly. This effect was undoubtedly due to some water being condensed or absorbed on the amber insulator through which the brass rod which formed a continuation of the gold-leaf system passed. The calcium chloride tube of course effectually remedied this trouble in so far as the deposition of moisture on the insulator was concerned, but at the same time it appeared to be the source of a peculiar and undesirable effect.

When a solution of monazite sand was connected with the apparatus and a determination made, it was found that the electroscopic readings decreased steadily, although slowly, with time, so that a constant value could not be reached (at least not in one hour). It did not appear probable that the change was occurring in the solution, for air had previously been passed through it for some time, and it was kept at constant temperature and volume. The effect, therefore, was most likely due to one or both of the following causes:

1. As the moist air flowed through the drying-tube, some moisture collected on the calcium chloride granules, thus filling in small interstices, and in general increasing the volume of material in the drying-tube. The speed of the air current would thus be diminished, hence the emanation would reach the ionization chamber less quickly and the electroscope would be discharged less rapidly. Therefore, as the wetting of the calcium chloride progressed slowly along the tube, the electroscopic readings would decrease accordingly.

2. As the wetting of the calcium chloride progressed along the tube, more and more moist surface would be exposed to the passing emanation, which would be, therefore, if at all absorbed by the water, increasingly lost in the drying-tube.

In order to discover whether the first possibility was, to any appreciable extent, the cause of the troublesome effect, we used a longer tube, fixed horizontally, into which only enough calcium chloride was placed to make a layer approximately filling the lower half of the tube. With this arrangement any change in volume due to deposition of water on the calcium chloride was negligible as compared with the total free space. The electroscopic readings, however, still decreased steadily as before. It appeared, therefore, that the second explanation was the cause of at least part of the trouble, i.e., that at least part of the emanation was was increasingly absorbed by the increasing area of moist surface. Such an effect constituted an objection applicable to all solid drying agents, and to water solutions, e.g., a saturated solution of calcium chloride. Concentrated sulphuric acid was not tried because of the likelihood that it would absorb thorium emanation much as it does radium emanation.

Condensers of various types were next tried. Since the moist air current carrying the emanation flows, during a determination, rather rapidly along the "line," it was necessary that the cooling-tubes of the condenser be either of small bore or very long, in order that all of the air be sufficiently cooled to condense the undesirable moisture. A very long tube was objectionable, because the rate of discharge of the electroscope decreases very rapidly with increase of length of line between the solution and the ionization chamber. This relation is due to the rapid decay of thorium emanation, its half-period being only approximately fifty-four seconds. It was essential, therefore, to devise a condenser with a short condenser tube, of small bore, which at the same time would not decrease the speed of flow of the air current. This problem was solved by passing the air through many short small-bore condensers combined in parallel. The condenser which we constructed is shown diagrammatically in Figure 4. It was found to be more unsatisfactory than the calcium chloride tube. The main trouble was that in a short time enough water condensed in the small tubes to partially close them all during the remainder of the experiment and intermittently to close one or more of them when water droplets of sufficient size were formed and drawn through. Other forms of condensers based on the same ideas were tried, e.g., an ordinary small condenser filled with glass beads.

In all cases the chief difficulty was the same, i.e., the small tubes or interstices soon filled more or less with water, producing continuous and spasmodic changes in the speed of flow of the air current.

Since the object of any method of drying the air stream was to prevent moisture from coming in contact with the insulator in the ionization chamber, and since none of the methods tried was entirely satisfactory, it was decided to do away with all drying materials and apparatus, and to allow the air stream to pass directly from the solution to the ionization chamber and to protect the insulator. An arrangement was therefore devised whereby the insulator was directly protected by calcium

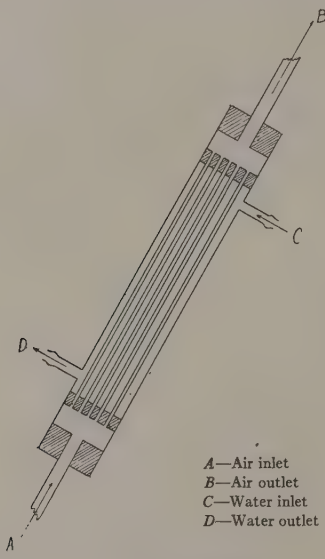


FIG. 4.—Multiple condenser

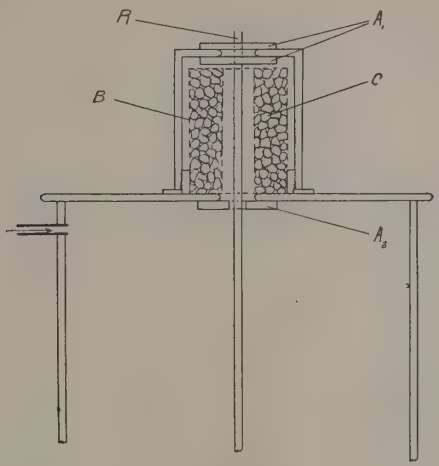
chloride. The modification of the apparatus is shown in Figure 5. The air-gap between the rod R and the amber A_2 constitutes a better resistance than amber itself. Circulation or diffusion of air through this air gap must be slight, and whatever air does reach the amber insulator A_1 is thoroughly dried by the calcium chloride in the wire-gauze basket, B. Determinations made with this modification of the apparatus were much more satisfactory in every way than those made when the air was dried before entering the ionization chamber, the main advantages being:

1. A shortening of the length of line between the solution and the ionization chamber, thus increasing the rate of discharge of the electroscope.

2. The rapid approach of the rate of discharge to a constant value.

This arrangement, although it did not appear to introduce errors of sufficient magnitude to effect results of the order of accuracy desired, was found to have the following objectionable features:

1. The calcium chloride basket had to be taken out and refilled after each determination.



R—Rod to electroscope
A_1—Amber insulator
B—Wire basket
C—Calcium chloride
A_2—Amber plug

FIG. 5.—Insulator protection (first form)

2. The capacity of the electroscope seemed to change very slowly and very slightly during a determination, probably on account of the gradual wetting of part of the calcium chloride (mainly near the air gap).

3. Uncontrollable and irregular effects (very slight) due to minute quantities of emanation getting into the "insulator chamber." (In this paper, by "insulator chamber" we mean the chamber fixed between the electroscope proper and the ionization chamber in the new modified apparatus.)

In the apparatus which we have finally adopted, these objectionable features are entirely eliminated by the use of the insulator protector

shown in Figure 6. Outside air is drawn very slowly (about twenty very small bubbles per minute) through the saturated calcium chloride solution S, hence through the calcium chloride tube C, the insulator chamber, and finally out through the air gap. The insulator is thus kept constantly in an atmosphere of dry air. At the same time no trouble of any kind can arise from circulation or diffusion of air into the insulator chamber because of the slow current constantly passing out. This insulator protector we have found to be perfect so far as the performance

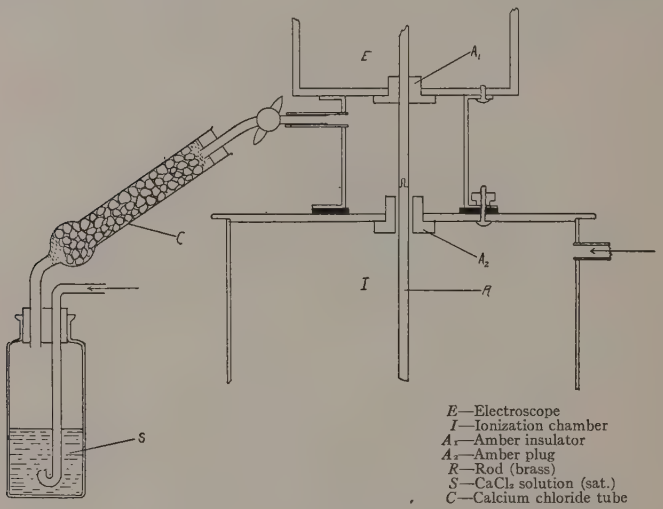


FIG. 6.—The insulator protection

of its function is concerned. It is extremely simple and requires practically no attention. Since air passes through them extremely slowly, the calcium chloride solution and the calcium chloride need to be replaced only after several months of use. The purpose of the calcium chloride solution is merely to furnish a means of observing the speed with which air is being drawn through the insulator protector. The results of the following experiment show the perfection of this part of the apparatus.

Several solutions of monazite sand which had been used in previous work were poured together, thoroughly mixed, and allowed to stand until the slight amount of suspended matter had settled. Three por-

tions of 75 c.c. each of the clear solution were then taken and the thorium content of each (relative to a standard) determined electroscopically. In each case the electroscopic readings became constant (within the reading error) within ten minutes (air had previously been passed through as usual), and then five more readings were taken and their average used in the calculations. The relative thorium contents of the three solutions as given by the determinations were:

1.0037×standard
1.0043×standard
1.0034×standard

The maximum variation is less than 0.1 per cent, and the mean variation from the mean is less than 0.04 per cent.

AN IMPROVEMENT IN THE SOLUTION

The results of the experiment described above showed that if the solutions were perfect very satisfactory results could be obtained. Actual determinations, however, with solutions prepared according to the method described in Part I, still gave results somewhat too inaccurate. This showed that either some material was lost on account of faulty methods of making the solutions, or that the slight amount of undissolved matter in the final solutions caused effects which we were unable to control and of a magnitude which could not be overlooked. It appeared probable that both of these causes were affecting our results. We attacked the problem of making a more nearly perfect solution first, however, since Cartledge[1] had pointed out the probable considerable magnitude of adsorption effects.

Qualitative tests showed that the undissolved material in the final "solution" was composed almost entirely of silica and ilmenite. Previous experiments (see Part I) to produce a betterment in the solution by treating the sand with hydrofluoric acid and by the introduction of calcium fluoride into the fusion had failed. A reconsideration of the problem now led us to believe that very probably those failures were due to one or more of the following causes: (1) low temperature of reaction; (2) loss of hydrogen fluoride before it had had time to complete its work. To eliminate these possible causes of failure the following experiment was carried out:

With 1.0 g. of monazite sand (India) was mixed a large excess, 5 g. of potassium hydrogen fluoride and 5 g. of metaphosphoric acid. The

[1] *Loc. cit.*

mixture was placed in a platinum crucible and brought slowly to the highest temperature of the Mekar burner. Considerable hydrogen fluoride was given off, most of it at the lower temperatures. The heating at the highest temperature was continued until no further reaction was apparent. The mass in the crucible then consisted of a clear viscous liquid, and a small coagulated mass of heavy solid material, presumably fluorides. The reason these fluorides were not decomposed was that the metaphosphoric acid had practically all been changed to potassium metaphosphate. We now had exactly the condition we had hoped to attain at this point, i.e., a fusion at a high temperature and containing fluorides. Continuing the heating, we now added 5 g. more metaphosphoric acid in small portions, allowing any reaction to become complete before adding another portion. In this way we succeeded in having hydrogen fluoride liberated slowly, and, to a degree, continuously, at a high temperature. After the last addition of metaphosphoric acid, the fused mass was allowed to cool, and then dissolved according to the method described in Part I. The solution thus produced was very much clearer than any previously made. In many cases the solutions made by this method have been so nearly perfect that it has been necessary to compare them with clear water in order to determine whether any turbidity was present.

This improved method of making the solution of monazite sand, combined with the change in the manner of protecting the insulator described in the preceding section, has so increased the accuracy with which determinations can be made that our method is now capable of giving results of the order of accuracy desired. The results of a series of analyses of several sands is given in a later section of this paper.

THE OPTIMUM PRESSURE GRADIENT

By the use of the regulator shown in Figure 1, the pressure may be so exactly controlled that inaccuracies due to variable pressure are negligible. Obviously, however, it was desirable to select that pressure at which the pressure coefficient of the rate of discharge of the electroscope is a minimum. A solution of monazite was therefore placed in the apparatus and the rate of discharge of the electroscope determined through the range of practical working pressures (manometer readings). The results were plotted, the electroscopic readings being taken as ordinates and the pressure (manometer) readings as absiccae. The curve, Figure 7, shows that the pressure coefficient of the rate of discharge of the electroscope is (for our apparatus) zero when the manometer reading is 11.5

cm. (of olive oil). (For the relation of the manometer to the remainder of the apparatus, see Fig. 3.) By working with the pressure corresponding to a manometer reading of 11.5 cm., we therefore practically eliminate all error due to pressure variation. But, as the curve shows quite clearly, the use of this pressure gives us at the same time another extremely desirable effect, i.e., the maximum rate of discharge obtainable. Thus,

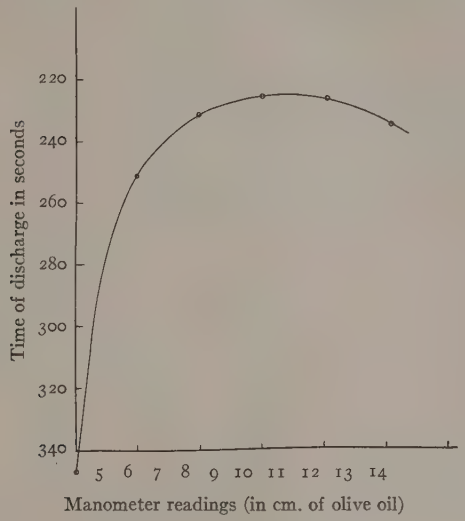


FIG. 7.—Pressure discharge curve

not only are errors due to variations of pressure eliminated, but we also get the greatest effect attainable with a given solution. Our method, therefore, becomes more rapid as well as more accurate.

THE USE OF A SINGLE VESSEL

At the very beginning of our work on this problem we pointed out that in an ideal method all of the operations with the sand would be carried out in a single vessel. In all of our analyses to date we have made a transfer of the viscous solution of the fused mass in 80 per cent orthophosphoric acid from the platinum crucible to the glass "solution vessel." This transfer should be eliminated if the maximum attainable accuracy and speed are desired, for the following reasons:

1. It is difficult to carry out successfully, even after much practice.

2. It consumes time, requiring about one-half hour.

3. Probable loss of some thorium X adsorbed on the surface of the platinum and practically inseparable from it even by washing a great number of times.

Almost undoubtedly the controlling error of the method lies in this transfer. It can easily be avoided by the use of a platinum vessel of such size and shape as will allow the final electroscopic determination to

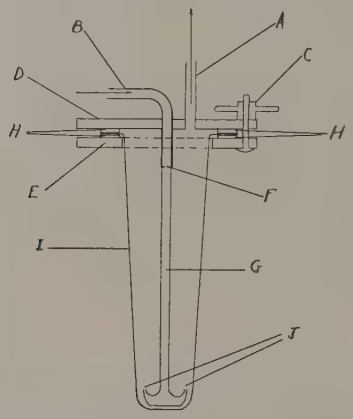


FIG. 8.—Platinum "solution vessel" and connections (actual size)

be made with the solution in it instead of in the special glass vessel we have used. We suggest, therefore, that if a great many analyses are to be made, a special platinum vessel be used. Figure 8 shows the dimensions which such a vessel should have, and a method of connecting the vessel to the "line."

RESULTS

In Table IV are given the results of a series of determinations showing the separate results of the triplicate analyses of each lot by our emanation method, and the average result from the triplicate analyses of each lot by the gravimetric method of Carney and Campbell.

The agreement of the results obtained by our emanation method with those obtained by the gravimetric method is very close.

COMPARISON OF METHODS

In order that a method of quantitative determination may be useful, it must give results sufficiently accurate for the purpose at hand. This our method does. In addition to accuracy, the next most desirable feature in a method is speed. In this respect our method is far superior to any other, a complete analysis by any gravimetric method requiring approximately twenty hours, whereas our method requires somewhat

TABLE IV

Lot No.	Source Monazite	Percentage ThO_2 Emanation Method	Average Percentage ThO_2 Emanation Method	Average Percentage ThO_2 Gravimetric Method
20	India	8.71 8.75 8.76	8.74	8.76
22	India	8.69 8.70 8.72	8.70	8.70
23	India	8.49 8.53 8.53	8.51	8.50
26	India	8.66 8.67 8.73	8.69	8.69
28	India	8.73 8.77 8.80	8.77	8.76
30	India	8.67 8.68 8.74	8.70	8.70
A	Brazil	6.37 6.38 6.40	6.38	6.38
B	Carolina	4.37 4.37 4.43	4.39	4.40

less than one-third that time. The technique involved is extremely simple except when the "transfer" (see Part I, p. 12) is made, and, as has been suggested above, that would probably not be done if a great many determinations were to be made.

The disadvantages inherent in the emanation method as compared with gravimetric methods are:

1. The apparatus required is somewhat costly.

2. The electroscope must be attached to a support practically free from vibration.

3. The electroscopic determinations must be made in a room free from unusual radio disturbances.

If a great many analyses were to be made, these disadvantages could be disregarded, since the saving in time attained by the use of this emanation method would soon more than compensate for the initial cost and for any inconvenience in installing and protecting the apparatus.

In concluding, the writer wishes to express his sincere appreciation of the valuable criticisms and helpful suggestions of Dr. Herbert McCoy, at whose suggestion this research was taken up.